Statistical Thermodynamics in Chemistry and Biology

16. Solvation and the transfer of molecules between phases

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The chemical potential describes the tendency of molecules to exchange and partition

This chapter:

- ▶ Some examples of colligative properties.
    - ▶ vapor pressure depression by solutes
    - ▶ freezing temperature depression (e.g. salt melts ice)
    - ▶ boiling temperature elevation (e.g. salt condenses boiling water)
    - ▶ osmotic pressure, partition coefficients, dimerization in a solvent
- ▶ The high-concentration component is called the solvent; the low-concentration component is called the solute.
- ▶ Two competing *driving forces*:
    - ▶ Molecules tend to move from regions with high concentration to low concentration to increase the entropy.
    - ▶ Also, molecules tend to move to regions where they have high chemical affinity.

Solvation

Solvation is the transfer of molecules between vapor and liquid phases

- ▶ Model system:
    - ▶ Liquid mixture of two components, *A* and *B*.
    - ▶ Suppose *B* is volatile, but *A* is not.
    - ▶ Constant *T*, *p*, N_A, N_B,

$$N_B^{\text{gas}} + N_B^{\text{mixture}} = N_B$$

- ▶ Two typical examples:
    - ▶ A gas, e.g. carbondioxide (*B*) dissolved in water (*A*).
    - ▶ A salt, e.g. sodium chloride (*A*) dissolved in water (*B*).
- ▶ At constant *p* and *T*, the condition for equilibrium is

$$\mu_B^{\text{gas}} = \mu_B^{\text{mixture}}$$

Lattice model for solvation

▶ Ideal gas (Eq. 11.50),

$$\mu_B^{\text{gas}} = k_B T \ln \frac{p_B}{p_{B,\text{int}}^o}$$

and for the mixture (Eq. 15.17),

$$\mu_B^{\text{mixture}} = \frac{zw_{BB}}{2} + k_B T \ln x_B + k_B T \chi_{AB} (1 - x_B)^2$$

$$\mu_B^{\text{mixture}} = \mu_B^o + k_B T \ln x_B + k_B T \chi_{AB} (1 - x_B)^2$$

▶ At equilibrium,

$$\frac{p_B}{p_{B,\text{int}}^o} = x_B \exp \left(\chi_{AB} (1 - x_B)^2 + \frac{zw_{BB}}{2k_B T} \right)$$
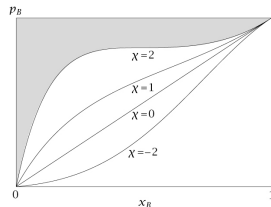
Lattice model for solvation
Part 2

▶ Rewrite as

$$p_B = p_B^o x_B e^{\chi_{AB}(1-x_B)^2}$$

where p_B^0 is the vapor pressure of the pure substance (Eq. 14.9),

$$p_B^o = p_{B,\text{int}}^o e^{\frac{zw_{BB}}{2k_BT}}$$

▶ See the figure for graphs with different χ_{AB}.

Two limiting cases

▶ Case 1: Salt in water
  ▶ B is the *solvent* and is volatile.
  ▶ $x_B \approx 1$,
  $$p_B = p_B^o x_B \qquad \text{and} \qquad \mu_B = \mu_B^o + k_B T \ln x_B$$
  which is Raoult's law.
  ▶ It is interpreted as an entropy effect.

▶ Case 2: Carbondioxide in water
  ▶ B is the *solute* and is volatile.
  ▶ $x_B \approx 0$,
  $$p_B = p_B^o e^{\chi_{AB}} x_B \qquad \text{and} \qquad \mu_B = \mu_B^o + k_B T \ln x_B + k_B T \chi_{AB}$$
  which is Henry's law.
  ▶ It is interpreted as an energy effect.
  ▶ Typical laboratory experiment for measuring χ_{AB} experimentally.

Henry's law

▶ Henry's law is in the literature written as
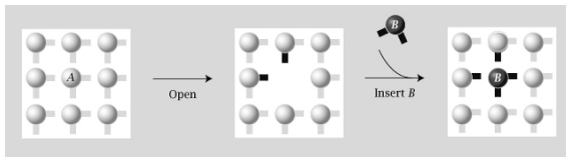
$$p_B = k_H x_B$$

where k_H is the Henry's law constant.

▶ Start at Eq. 16.2 (and $x_B \approx 0$),

$$\frac{p_B}{p_{B,\text{int}}^o} = x_B \exp\left(\chi_{AB} + \frac{z w_{BB}}{2 k_B T}\right) = x_B \exp\left(\frac{z}{k_B T}\left(w_{AB} - \frac{w_{AA}}{2}\right)\right)$$

which gives

$$k_H = p_{B,\text{int}}^o \exp\left(\frac{z}{k_B T}\left(w_{AB} - \frac{w_{AA}}{2}\right)\right) = p_{B,\text{int}}^o \exp\left(\frac{\Delta h_{\text{solution}}^o}{k_B T}\right)$$

▶ $\Delta h_{\text{solution}}^o$ (to be exact $\Delta U / N$) describes the process in the figure below

Solutes raise the boiling temperature of a solvent

▶ The boiling point, T_b, is the temperature where the vapour pressure equals the atmospheric pressure (normally 1 atm). (Not shown in this course).

▶ First assume that we have a pure liquid (no salt) with a boiling point, T_{b0} at a pressure, p_{atm},

$$p_{atm} = p_{B,int}^o \exp\left(\frac{zw_{BB}}{2RT_{b0}}\right)$$

(it does not matter if we use R or k_B, but could have been used consistently.).

▶ Secondly, we have a solution with a salt concentration, x_A. Using Raoult's law, $x_B \approx 1$,

$$p_{atm} = p_{B,int}^o x_B \exp\left(\frac{zw_{BB}}{2RT_{b1}}\right)$$

▶ Putting these two equations equal,

$$\ln x_B = \frac{zw_{BB}}{2R}\left(\frac{1}{T_{b0}} - \frac{1}{T_{b1}}\right)$$

Solutes raise the boiling temperature of a solvent

Part 2

▶ First, a Taylor expansion around T_{b0},

$$\frac{1}{T_{b0}} - \frac{1}{T_{b1}} \approx \frac{1}{T_{b0}} - \left(\frac{1}{T_{b0}} + (T_{b1} - T_{b0}) \frac{-1}{T_{b0}^2} \right) = \frac{\Delta T}{T_{b0}^2}$$

▶ Secondly (see exercise E16.1),

$$\ln x_B = \ln(1 - x_A) \approx -x_A - \frac{x_A^2}{2} - \frac{x_A^3}{3} - \ldots$$

▶ Finally, introducing

$$\Delta h_{\text{vap}}^o = \Delta h_{\text{gas}}^o - \Delta h_{\text{liq}}^o = \frac{-zw_{BB}}{2}$$

gives the final result commonly found in text-books. (Why is $\Delta T > 0$?)

$$\Delta T = \frac{RT_{b0}^2 x_A}{\Delta h_{\text{vap}}^o}$$

▶ The result is explained as an entropy effect. The result is generic for any solute since it does not depend on w_{AA} and w_{AB} (but it depends on w_{BB}). Easy to generalize to a more sophisticated model.

Units of concentration

▶ Sometimes other units are used than molar fractions, x_A

$$x_A = \frac{n_A}{n_A + n_B} \approx \frac{n_A}{n_B}$$

▶ The molarity or concentration, c_A (in mol solute/liter solvent) is

$$c_A = \frac{n_A}{V}$$

▶ The molality, m_A, (in mol solute/kg solvent) is,

$$x_A \approx m_A M_B$$

where M_B is the molar mass (g/mol).

▶ If only the linear term is included for the change in boiling point,

$$\Delta T = K_b m_A = \frac{RT_b^2 M_B}{\Delta h_{\text{vap}}^o} m_A$$

where K_b is a constant for boiling that only depends on properties for the pure solvent.

Solutes lower the freezing point of a solvent

▶ Assuming that the salt is only present in liquid water and not in ice, we get similar expressions,

$$\Delta T_f = T_f - T = \frac{k_B T_f^2}{\Delta h_{\text{fus}}^o} \left(x_A + \left(\frac{1}{2} - \chi_{AB} \right) x_A^2 + \dots \right)$$

and

$$T_f - T = K_f m_A$$

where T_f is the freezing point of the pure liquid.

▶ Not derived. We also indicate how higher-order corrections enter, which would show up analogously for the boiling point. See Exam Aug. 2017:3 for an exercise on these correction terms.

Osmotic pressure

Semipermeable membranes

- ▶ Model system: pure liquid *B* separated from a mixture of *A* and *B* by a semipermeable membrane that lets *B* but not *A* pass freely.
- ▶ Molecules *B* will be drawn from the pure liquid to the mixture to increase the entropy.
- ▶ This can be countered by
  - ▶ Increasing the pressure of the mixture
  - ▶ or accumulate extra volume on the top, which will give an extra hydrostatic pressure because of its weight.
- ▶ This additional pressure is termed the osmotic pressure, π.
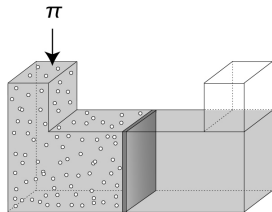
Osmotic pressure

Semipermeable membranes, part 2
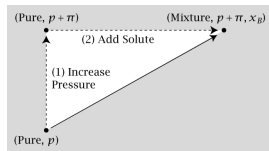
▶ The condition for equilibrium becomes (at constant T),

$$\mu_B^{\mathrm{pure}}(p) = \mu_B^{\mathrm{mixture}}(p + \pi, x_B)$$

▶ Use that the free energy is a state function, and divide the process into two steps (see figure).

▶ First step $p \to p + \pi$,

$$\mu_B^{\mathrm{pure}}(p + \pi) = \mu_B^{\mathrm{pure}}(p) + \int_p^{p+\pi} \frac{\partial \mu_B}{\partial p} dp$$

▶ Use the Maxwell relation: $\frac{\partial \mu_B}{\partial p} = \frac{\partial V}{\partial N_B} = v_B$,

$$\mu_B^{\mathrm{pure}}(p + \pi) = \mu_B^{\mathrm{pure}}(p) + \pi v_B$$

Osmotic pressure

Semipermeable membranes, part 3

▶ For the second step (creating the mixture) using Raoult's law,

$$\mu_B^{\text{mixture}}(p + \pi, x_B) = \mu_B^{\text{pure}}(p + \pi) + RT \ln x_B$$

▶ For both steps,

$$\mu_B^{\text{mixture}}(p + \pi, x_B) = \mu_B^{\text{pure}}(p) + \pi v_B + RT \ln x_B$$

▶ Thus at equilibrium ($\mu_B^{\text{mixture}}(p + \pi, x_B) = \mu_B^{\text{pure}}(p)$)

$$-\pi v_B = RT \ln x_B$$

▶ Again use,

$$\ln x_B = \ln(1 - x_A) \approx -x_A - \frac{x_A^2}{2} - \frac{x_A^3}{3} - \dots$$

▶ Finally, the osmotic pressure is given in terms of the concentration as (using the linear term only),

$$\pi = \frac{RT}{v_B} x_A \approx \frac{n_A RT}{n_B v_B} = \frac{n_A RT}{V} = c_A RT$$

▶ Again, a *text-book* result is obtained, that we can extend systematically with the lattice model.

Partition coefficients

Solutes can transfer from one solvent to another

▶ Model system: Two immiscible solvents A and B (e.g. oil and water). A solute s can transfer between the two solvents.

▶ The partition coefficient, K_A^B, is defined as

$$K_A^B = \frac{x_s^B}{x_s^A}$$

where x_s^A is the molar fraction of s in solvent A.

▶ Condition for equilibrium,

$$\mu_s^A = \mu_s^B$$

which gives (for $\frac{\mu_s^A}{k_B T} = \frac{\mu_s^B}{k_B T}$) using Eq. 15.17 for μ of a solution,

$$\frac{zw_{ss}}{2k_B T} + \ln x_s^A + \chi_{sA}\left(1 - x_s^A\right)^2 = \frac{zw_{ss}}{2k_B T} + \ln x_s^B + \chi_{sB}\left(1 - x_s^B\right)^2$$

▶ The final result becomes,

$$\ln K_A^B = \ln \frac{x_s^B}{x_s^A} = \chi_{sA}\left(1 - x_s^A\right)^2 - \chi_{sB}\left(1 - x_s^B\right)^2 \approx \chi_{sA} - \chi_{sB}$$

where we in the last have used that $x_s^A \to 0$ and $x_s^B \to 0$.

Model for dimerization

▶ Dimerization is the equilibrium between a solvated dimer, *AB*, and two solvated monomers *A* and *B* (see figure). The equilibrium constant is defined as

$$K_{\text{dimer}} = \frac{x_{AB}}{x_A x_B}$$

▶ Approximation: All three species are at infinite dilution in a solvent *s*.
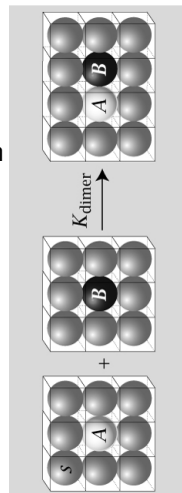
▶ At constant p and T,

$$dG = \mu_A dN_A + \mu_B dN_B + \mu_{AB} dN_{AB} = 0$$

▶ Conservation of *A* and *B* leads to

$$dN_{AB} = -dN_A = -dN_B$$

▶ At equilibrium, $dG = 0$,

$$(-\mu_A - \mu_B + \mu_{AB})\, dN_{AB} = 0 \quad \Rightarrow \quad \mu_{AB} = \mu_A + \mu_B$$

Model for dimerization
Part 2

▶ Rewrite the equilibrium condition as

$$\left(\frac{\mu_{AB}^o}{k_B T} + \ln x_{AB} \right) = \left(\frac{\mu_A^o}{k_B T} + \ln x_A \right) + \left(\frac{\mu_B^o}{k_B T} + \ln x_B \right)$$

so that

$$\ln K_{\mathrm{dimer}} = \ln \left(\frac{x_{AB}}{x_A x_B} \right) = -\frac{1}{k_B T} \left(\mu_{AB}^o - \mu_A^o - \mu_B^o \right) = -\frac{1}{k_B T} \Delta \mu^o$$

▶ Using the notation for μ_A^o (and μ_B^o) (in line with Eq. 15.17),

$$\frac{\mu_A^o}{k_B T} = \frac{z w_{AA}}{2 k_B T} + \chi_{sA} - \ln q_A = \frac{z}{k_B T} \left(w_{sA} - \frac{w_{ss}}{2} \right) - \ln q_A$$

where the molecular partition functions, q_A, has been included and $\chi_{sA} \approx \chi_{sA}(1 - x_A)^2$

Model for dimerization
Part 3

- ► We also need μ_{AB}^o, which is obtained from the free energy of the process in the figure.
- ► Consider a two-site cavity surrounded by a first shell of $2(z-1)$ solvent molecules.
- ► The energy cost of opening a two-site cavity is thus $-w_{ss}(z-1)$ (see ch. 14)
- ► Insertion of an A molecule gives $(z-1)\,w_{sA}$; insertion of B molecule gives $(z-1)\,w_{sB}$; a dimer is formed with the energy w_{AB},

$$\frac{\mu_{AB}^o}{k_B T} = \frac{z-1}{k_B T}\left(w_{sA} + w_{sB} - w_{ss}\right) + \frac{w_{AB}}{k_B T} - \ln q_{AB}$$
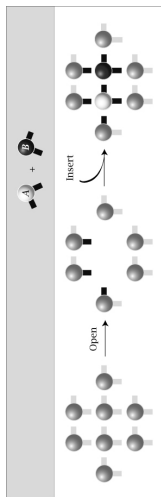
Model for dimerization

Part 4

▶ The equilibrium constant becomes,

$$\ln K_{\text{dimer}} = -\frac{\Delta\mu^o}{k_B T} = \frac{w_{sA} + w_{sB} - w_{ss} - w_{AB}}{k_B T} + \ln\left(\frac{q_{AB}}{q_A q_B}\right)$$

$$= \frac{1}{z}\left(\chi_{sA} + \chi_{sB} - \chi_{AB}\right) + \ln\left(\frac{q_{AB}}{q_A q_B}\right)$$

▶ Note that q_{AB} may be very different from $q_A q_B$. For example, if A and B are rare gas atoms, they only include a translational contribution to q. However, q_{AB} includes also vibrational and rotational contributions.

▶ Dimerization in a solvent can be driven by many different "effects". Strong interactions between A and B or between s and s will favour dimerization. Strong interactions between A and s or between B and s will disfavour dimerization.

▶ The hydrophobic effect (the dimerization of two unpolar (oil) molecules in water) as an example. In this case, *water likes water*, i.e. a large w_{ss} favour dimerization.

Summary

- ▶ Many different phenomena have been considered based on the lattice model:
  - ▶ Solvation
  - ▶ How solvation can raise the boiling temperature and lower the freezing temperature
  - ▶ Osmotic pressure - semipermeable membranes
  - ▶ Partition of solute molecules between two phases - partition coefficients
  - ▶ Model for dimerization in solution

E16:2 (Exam Dec 2008:1)

We looked at a) and b) in chapter 14

Vapour pressure

a) The vapour pressure for a pure solvent may be written as

$$p = p_{int}^o e^{\frac{\beta z w_{AA}}{2}}$$

Explain the various variables and constants in the equation. Which are the two fundamental approximations in this model for the vapour pressure, and what are the main limitations in each of the approximations?

b) What happens with the vapor pressure at high and low temperatures, and at strong and weak interactions between the liquid particles, respectively? Explain the results.

c) What is the difference between an ideal and a regular solution? For a regular solution with components *A* and *B*, where only *A* forms a vapour, discuss the condition for that the vapour pressure, p_A, increases or decreases as compared to an ideal solution?

E15.4. (Exam June 2013:2)

a) Self-assembly is used in nanoscience to construct devices on a molecular scale. Here we use a surface as a carrier material, and we have two types of molecules A and B that we expect to assemble on the surface according to the pattern in the figure, i.e. with only $A - B$ interactions.

A	B	A	B	A	B	A	B
B	A	B	A	B	A	B	A
A	B	A	B	A	B	A	B
B	A	B	A	B	A	B	A
A	B	A	B	A	B	A	B

E15.4. (Exam June 2013:2)
Part 2

We have $N_A = N_B$ molecules which can be assumed to be a large number. The temperature is 300 K. Calculate the free energy difference, ΔF, between the pattern in the figure and a random distribution of the molecules on the surface in terms of the interaction energies. We use w_{AA}, w_{BB} and w_{AB} for the intermolecular interactions and w_{As} and w_{Bs} for the molecule-surface interactions. Is it important in this task to assume that we have a large number of molecules? Motivate the answer.

E15.4. (Exam June 2013:2)

Part 3

b) The Boltzmann distribution may be written as

$$p_j = \frac{g_j e^{-\beta E_j}}{Q}$$

where g_j is the degeneracy (multiplicity) of energy level j. Show by using this equation as a starting point that the ratio between the probabilities to be at two energy levels can be given in terms of ΔF as

$$\frac{p_j}{p_i} = e^{-\beta \Delta F}$$

What is the condition in terms of the interaction energies to get a ratio larger than 1000/1 between the correct assembly (in the figure) and a random configuration? Does the result depend on the number of molecules? Motivate the answer. Here we can assume that $w_{AA} = w_{BB}$. This condition may be difficult to achieve for some systems, so can you suggest some approaches to improve the preference for the correct assembly?